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Fate of Trace and Minor Constituents of Coal During Gasification

Institute of Gas Technology, Chicago, Ill

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Industrial Environmental Research Lab, Research Triangle Park, N C

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FATE OF TRACE AND MINOR CONSTITUENTS OF COAL DURING GASIFICATION

by

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ABSTRACT

This report covers the continuation of a study initiated by the Environmental Protection Agency to investigate the fate of trace constituents of coal during the coal gasification process for the production of pipeline-quality gas.

The present work concentrates on the fate of 39 minor and trace elements of Montana lignite and Illinois No. 6 bituminous coal during gasification in a 0.1 m (4-inch) reactor of an IGT process development unit (PDU) as well as a Montana lignite gasification run conducted at HYGAS pilot plant. The samples available for this study were limited to coal feed and coal residue samples of the pretreatment (in case of bituminous coal) and hydrogasification stages of the above units.

Examination of the data, obtained in this study, indicate that significant loss of volatile trace elements from coal occurs during coal gasification, regardless of the feed type or the size of the gasification unit. The elements so removed, will likely concentrate in the quench water and acid-gas scrubber, thus requiring a systematic recovery and disposal of the accumulated elements.

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INTRODUCTION

This study is the continuation of a program initiated by the Environmental Protection Agency in May of 1972 to investigate the fate of 11 trace elements, contained in a Pittsburgh No. 8 bituminous coal, during gasification.[4]

The scope of the program was subsequently expanded (under Contract No. 68-02-1307) to cover the investigation of a total of 39 trace and minor elements in two series each, of Montana lignite and Illinois No. 6 bituminous coal samples and residues obtained from the past hydrogasification runs conducted in an IGT 0.1 m process development unit (PDU) - also referred to as 4-inch (reactor) bench-scale unit. The expanded program (commencing in January, 1973) also included the analysis of a series of feed and solid residue samples from a HYGAS coal gasification run, using Montana lignite.

An amendment to the contract required the preparation of a comprehensive test plan which consisted of the preparation of a preliminary plan for the eventual execution of an orderly test program involving all the streams of a HYGAS-based commercial plant - but included no actual sampling or analysis. The above test plan has been completed and reported under a separate cover.[10]

The contents of this report are concerned only with the analysis of solid samples and include no sampling or analysis of the gaseous and liquid streams of either PDU or HYGAS pilot plant.

CHAPTER I. EXPERIMENTAL

A. The HYGAS Process

The HYGAS Process shown in Figure 1, was developed by the Institute of Gas Technology (Chicago) for the U.S. Department of the Interior's Office of Coal Research (now ERDA) and the American Gas Association, and has reached the pilot plant stage. The pilot plant is designed to process 68 metric tons of coal and produce 42,500 cubic meters of pipeline quality gas daily.

This process can operate with any rank or type of coal and is tailored for the maximum thermal efficiency by optimizing the direct formation of methane in the reactor. High temperature (650 to 760°C in the first stage, and 870 to 980°C in the second stage) guarantee reasonable reaction rates, and high pressure (about 75 atm in both stages) increases equilibrium methane yield.

The most active fraction of coal is hydrogasified to form methane, while the less active fraction is used to generate hydrogen in support of the reactions. The raw gas from the hydrogasifier contains substantial amounts of carbon monoxide and hydrogen. These are converted indirectly to methane during catalytic clean-up methanation, boosting the heating value of the gas, and reducing carbon monoxide content to below 0.1%.

In the HYGAS pilot plant operations, coal is ground to -8 mesh size and fed into a pretreater if the feed is an agglomerating coal; otherwise it is fed directly to the slurry preparation section if coal is non-agglomerating. The caking tendency of coal is destroyed in the pretreater by mild surface oxidation of the coal particles, using air as the oxidant.

All types of coal, with or without pretreatment, are slurried with a by-product aromatic oil and then pumped to a pressure of 83 atm and moved to the reactor. The oil is evaporated in a slurry drier, and later condensed and recycled. The dried coal is moved to the bottom of the first hydrogasification stage.

In the first stage of reactor, coal enters a high-velocity rising stream of hot gases that originate in the lower, second stage. As the solids/gas mixture rises, the coal is rapidly heated by dilute-phase contact with hot

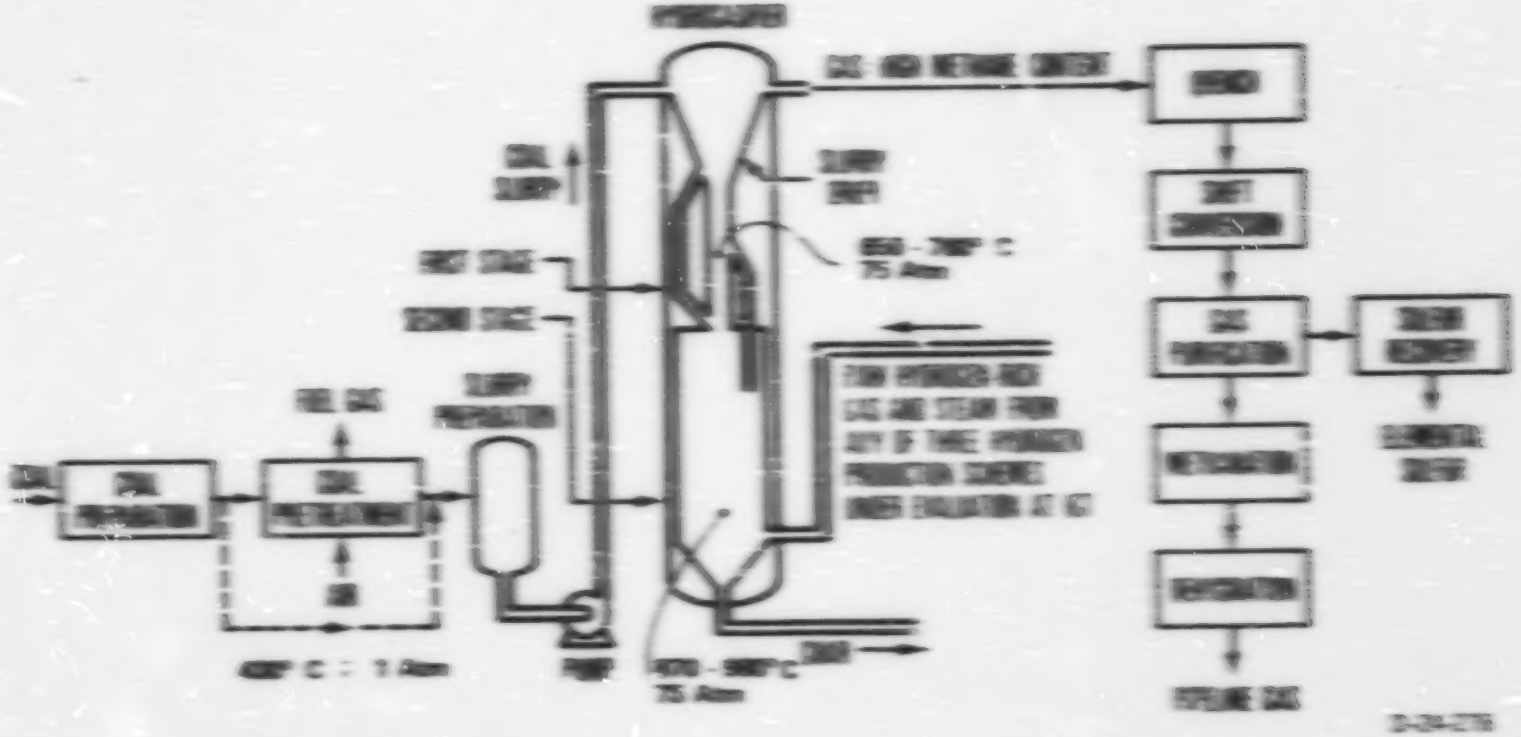

Figure 1. THE IGT HYGAS PROCESS

reaction gases. At the top of this riser-reactor, gas velocity is reduced, solids drop out, and gas continues upward, drying incoming coal in the slurry drier. Hot char is channeled downward to a dense-phase fluidized bed in the second, high-temperature reactor stage. Hot gases pass through the fluidized bed contacting char with good mixing. Organic carbon remaining in char after this stage can be used at other process points to produce both hydrogen and heat required in the HYGAS conversion process.

Subsequent process steps include quench, shift to a 3:1 ratio of hydrogen to carbon monoxide, gas purification, methanation, and drying before the final product emerges as high-Btu SNG.

B. Sample Selection

After the examination of data from a large number of gasification runs conducted in IGT process development unit (PDU) on Montana lignite and Illinois No. 6 bituminous coal, four series of coal feed and residue samples were selected. The samples were collected from two similar hydrogasification runs on each of the above two coal types and consisted of feed, intermediate residue, and the final residue samples. These samples and their gasification sequences are outlined in Table 1.

An additional series of feed and residue samples were also obtained from the steady-state periods of HYGAS run No. 27 on Montana lignite, as listed in Table 2.

The scope of this work was limited to the analysis of coal feed and solid residue samples only and did not include any liquid or gaseous samples.

C. Analytical Results

Proximate and ultimate analyses for the above 28 samples are reported in Tables 3, 4, and 5. Trace and minor element concentrations are reported in Tables 6, 7, and 8. The reported values for the trace and minor elements, are calculated on the coal-feed basis.

The average values of each element, in feed and final residue samples (from similar gasification runs conducted on the same type of coal) are reported in Table 9 along with percent change (loss or gain) of each element during gasification. The percent change values are calculated from the

Table I. LIST OF SELECTED COAL GASIFICATION SAMPLES FROM(0.1 M PEACTOR) IGT PROCESS DEVELOPMENT UNIT

I. Illinois No. 6 Bituminous Coal*

A. First Series:

F-FP-99 — Fed to Pretreater → B-FP-9; or F-HT-154 — Fed to Hydro-gasifier → B-HT-156

B. Second Series:

F-FP-105 — Fed to Pretreater → B-FP-105 or F-HT-155 — Fed to Hydro-gasifier → B-HT-155

II. Montana Lignite*

A. First Series:

F-HT-254 — Fed to 1st Stage Hydrogasifier → B-HT-254 or F-HT-256-1 — Fed to 2nd Stage Hydrogasifier → B-HT-256-1

B. Second Series:

F-HT-255 — Fed to 1st Stage Hydrogasifier → B-HT-255 or F-HT-256-2 — Fed to 2nd Stage Hydrogasifier → B-HT-256-2

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* Each sample in these two series is prefixed by a letter F or B (designating feed or residue, respectively) followed by letters FP or HT (denoting a pretreatment or hydrogasification run, respectively) and is, finally, suffixed by the corresponding serial run number.

* This feedstock does not agglomerate in the hydrogasifier, therefore, it has not been pretreated, but it has been hydrogasified in two stages of increasing severity.

Table 2. LIGNITE SAMPLES SELECTED FROM A 4-DAY STEADY-STATE PERIOD OF HYGAS RUN NO. 27

Sample Designation*	Date	Time
F-27-300	5-3-74	05:40
R-27-329	5-3-74	04:00
R-27-330	5-3-74	12:05
R-27-331	5-3-74	16:00
R-27-332	5-3-74	20:00
F-27-344	5-4-74	09:30
R-27-366	5-4-74	12:15
F-27-379	5-5-74	08:00
R-27-381	5-5-74	08:50
R-27-406	5-5-74	12:20
R-27-408	5-6-74	00:20
F-27-410	5-6-74	02:20
R-27-411	5-6-74	04:05
R-27-412	5-6-74	08:05
F-27-428	5-6-74	08:45
R-27-439	5-6-74	12:12

* Letter prefixes F and R designate feed or residue samples, respectively.

Table 3. PROXIMATE AND ULTIMATE ANALYSES OF MONTANA LIGNITE SAMPLES FROM RUN 6.1 in PDU GASIFICATION MODE.

Proximate, As Received	F-RT-254	F-RT-256-1	B-RT-256-1	F-RT-255	F-RT-256-2	B-RT-256-2
Moisture	12.1	2.0	0.8	11.6	1.3	0.8
Volatile Matter	36.8	9.1	7.6	36.3	5.4	7.1
Ash	9.2	18.9	23.4	8.3	18.8	25.3
Fixed Carbon (by difference)	42.7	70.0	68.2	43.8	74.5	66.8
Total	100.8	100.0	100.0	100.0	100.0	100.0
Ultimate, Dry Basis						
Ash (corrected for SO_3)	10.45	19.38	23.62	9.38	19.09	25.52
Carbon	62.3	73.6	70.3	62.7	72.4	64.1
Hydrogen	4.38	1.76	1.09	4.09	1.65	0.95
Sulfur	1.38	0.84	0.62	4.80	1.23	0.80
Nitrogen	0.66	0.57	0.39	0.96	0.66	0.36
Oxygen (by difference)	21.12	3.97	3.74	22.97	3.89	3.27
Total	100.00	100.00	100.00	100.00	100.00	100.00

Table 4. PROXIMATE AND ULTIMATE ANALYSES OF ILLINOIS NO. 6 BITUMINOUS COAL SAMPLES, FROM HOT G.I.m. PDU CASEFIL...TION RUNS.

Proximate, As Received	F-FP-99	F-HT-156	B-HT-156	F-FP-185	F-HT-255	B-HT-255
Moisture	13.3	1.4	0.3	9.4	1.1	0.5
Volatile Matter	33.0	22.7	1.0	33.7	23.0	4.1
Ash	6.9	11.3	22.1	9.6	12.9	20.5
Fixed Carbon (by difference)	46.9	64.6	76.6	47.3	63.0	74.9
Total	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate,Dry Basis						
Ash (corrected for SO_3)	10.10	11.48	22.20	10.58	13.98	20.68
Carbon	70.1	78.3	74.7	71.1	66.6	77.0
Hydrogen	4.88	3.58	0.59	4.62	5.25	1.17
Sulfur	3.74	3.33	1.78	3.90	3.45	1.44
Nitrogen	1.07	1.20	0.42	1.01	1.34	0.56
Oxygen (by difference)	10.11	10.11	0.32	8.80	10.10	—
Total	100.00	100.00	100.00	100.00	100.00	100.00

Table 5. PROXIMATE AND ULTIMATE ANALYSES OF MONTANA LIGNITE SAMPLES FROM HYDAS BOR NO. 27

	Feed Samples					Spear Char (Residue) Samples		
Proximate (as received)	F-380	F-382	F-379	F-458	F-459	S-329	S-330	S-331
Moisture	10.8	10.6	11.5	9.1	9.4	2.1	2.7	2.2
Volatile Matter	34.2	33.8	34.6	35.2	36.5	16.1	17.4	11.9
Ash	9.2	10.3	10.7	10.7	9.9	27.7	29.4	39.1
Fixed Carbon (by difference)	45.8	45.3	43.2	45.0	44.2	54.1	50.5	46.8
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate (dry basis)								
Ash (corrected for SO_3)	10.33	11.49	12.11	11.77	10.97	28.26	30.24	39.94
Carbon	63.4	62.8	62.3	61.9	62.6	62.6	59.5	54.2
Hydrogen	4.23	4.06	3.87	4.09	4.14	2.48	2.57	1.64
Sulfur	0.67	1.03	1.14	0.78	0.80	0.64	0.67	0.48
Nitrogen	0.92	0.91	0.91	0.92	0.93	0.65	0.69	0.17
Oxygen (by difference)	20.45	20.69	19.67	20.54	20.57	6.44	6.33	3.64
Total	100.00	100.00	100.00	100.00	100.00	100.30	100.00	100.00

Table 5, Cont. PROXIMATE AND ULTIMATE ANALYSES OF MONTANA LIGNITE SAMPLES FROM HYGAS RUN NO. 27

	Spent Char (Residue) Samples							
Proximate (as received)	R-332	R-356	R-385	R-406	R-408	R-411	R-412	R-439
Moisture	2.4	4.1	7.2	4.8	1.7	2.2	3.2	1.7
Volatile Matter	18.7	25.5	22.6	23.1	12.6	10.1	10.8	25.5
Ash	25.7	21.1	23.5	23.4	32.?	36.2	28.0	33.2
Fixed Carbon (by difference)	52.2	49.3	46.7	48.5	52.8	51.5	58.8	49.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate (dry basis)								
Ash (corrected for SO_3)	26.35	22.03	25.35	24.37	33.50	37.02	29.57	33.72
Carbon	63.1	62.8	66.5	63.9	58.8	57.3	60.0	57.5
Hydrogen	2.75	3.32	2.50	2.85	2.02	1.57	2.61	1.98
Sulfur	0.66	0.85	0.77	0.76	0.59	0.31	0.70	0.49
Nitrogen	0.77	0.95	0.73	0.84	0.49	0.24	0.63	0.47
Oxygen (by difference)	6.37	10.05	4.15	7.36	4.61	3.56	7.01	5.80
Total	100.00	100.00	100.00	100.00	100.01	100.00	100.00	100.00

Table 6. CONCENTRATION OF MINOR AND TRACE ELEMENTS IN FEED AND RESIDUE SAMPLES OF PDU GASIFICATION RUNS OF MONTANA LIGNITE, CALCULATED ON THE FEED BASIS.

Elements, ppm	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Antimony	0.10	1.0	0.10	0.10	0.10	0.07
Arsenic	10	10	10	10	10	10
Barium	50	50	50	50	50	50
Beryllium	0.05	1.1	0.05	0.05	0.05	0.07
Bismuth	1.0	1.1	1.0	1.0	1.0	1.0
Boron	100	100	100	100	100	100
Cadmium	0.50	0.67	0.50	0.50	0.50	0.50
Calcium	1,000	1,000	1,000	1,000	1,000	1,000
Chlorine	1,000	1,000	1,000	1,000	1,000	1,000
Chromium	10	10	10	10	10	10
Cobalt	5.0	5.7	5.0	5.0	5.0	5.0
Copper	10	10	10	10	10	10
Fluorine	50	83	50	50	50	50
Germanium	5.0	5.3	5.0	5.0	5.0	5.0
Iron	10,000	10,000	10,000	10,000	10,000	10,000
Lead	5.0	10	5.0	5.0	5.0	7.0
Lithium	50	50	50	50	50	50
Magnesium	500	810	500	500	500	500
Manganese	50	50	50	50	50	50
Mercury	0.07	0.070	0.034	0.016	0.004	0.004
Molybdenum	5.0	7.5	5.0	7.0	5.0	7.0
Nickel	10	10	10	10	10	10
Nitrogen	10,000	10,000	11,000	11,000	1,000	1,000
Potassium	1,000	1,100	1,100	1,100	1,000	1,000
Sodium	0.70	0.70	0.70	0.70	0.70	0.70
Selenium	10	10	10	10	10	10
Silicon	20,000	21,000	19,000	21,000	19,000	21,000
Silver	0.11	0.10	0.050	0.017	0.011	0.010
Sodium	1,000	1,000	1,000	1,000	1,000	1,000
Strontium	10	10	10	10	10	10
Sulfur	17,000	10,000	19,000	19,000	0.100	1,000
Tellurium	0.5	1.7	0.5	0.5	0.5	1.0
Thorium	1.1	1.1	1.1	1.1	1.1	1.1
Tin	1.0	4.0	1.0	4.0	1.0	0.71
Titanium	100	400	100	400	100	100
Vanadium	0.10	0.10	0.10	0.10	0.10	0.10
Ytterbium	10	10	10	10	10	10
Zinc	10	10	10	10	10	10
Zirconium	10	10	10	10	10	10

a. Insufficient sample

Table 7. CONCENTRATION OF MINOR AND TRACE ELEMENTS IN FEED AND RESIDUE SAMPLES OF PDU GASIFICATION RUNS OF MONTANA LIGNITE, CALCULATED ON THE FEED BASIS.

Elements, ppm						
Antimony						
Arsenic						
Barium						
Beryllium						
Bismuth						
Boron						
Cadmium						
Cyanide						
Chlorine						
Chromium						
Cobalt						
Copper						
Fluorine						
Germanium						
Iron						
Lead						
Lithium						
Magnesium						
Manganese						
Mercury						
Molybdenum						
Nickel						
Nitrogen						
Potassium						
Samarium						
Selenium						
Silicon						
Silver						
Sodium						
Strontium						
Sulfur						
Tellurium						
Thorium						
Tin						
Titanium						
Tungsten						
Uranium						
Vanadium						
Yttrium						
Zinc						
Zirconium						

* Due to possible contamination, this result was not used

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[illegible] [illegible] [illegible] [illegible] [illegible]

listed average elemental concentrations.

Extensive information, regarding the detailed analytical procedures developed for this project, appear in Chapter 23 of this report.

D. Discussion of the Results

In general, the samples obtained from the PDU hydrogasification runs were more suitable for this type of study than the HYGAS samples. The PDU hydrogasification uses a dry-fed and dry-discharged process causing no significant cross contamination from one run to the next. Whereas, the HYGAS plant uses a coal-toluene slurry to feed the coal and a coal-water slurry to discharge the residue, causing contamination of discharged samples by the accumulated soluble salts in the recycled process water. This is particularly evident in a two-fold increase in chloride concentration for HYGAS samples (see Table 9).

In addition to errors from contamination, the HYGAS residue samples showed a great variation in ash content from a low of 22.03 percent to a high of 39.94 percent, whereas the spread for the ash in feed samples was 10.33 percent to 12.11 percent (see Table 3). The spread in the ash (and consequently the trace element) content of the HYGAS residues are caused by periodic process up-sets.

Because of the above mentioned difficulties in obtaining representative samples from HYGAS operation, we do not consider the reported data for HYGAS as reliable as the PDU data. Nevertheless, all reported data show the same general trend in removal of volatile elements during gasification, with a few exceptions. Deviating from this trend are the elements Ca, Cu, Ag, Sr, and Sn, which exhibit substantially different behavior during the gasification of the two feedstocks under discussion.

Considering the data presented in Table 9 for the PDU samples only, it is apparent that the elements Ca, Ag, and Sn, show significant loss during the gasification of Illinois No. 6 bituminous coal, but show 100% retention in the residue samples of Montana lignite. The order is completely reversed, however, with Cu and Sr. This behavior can not be assigned to experimental errors, since the results for the elements involved showed good

repeatability for PDU samples from one similar sample to the next and also among the replicates of the same sample (of the order of 5%). In other words, the differential losses of these elements from the two feed types seem to be quite real and may be due to the differences in chemical forms (in which they occur) having different resistance to the reducing atmosphere of the hydrogasifier for hydride formation, or simply, this is the case of differential volatility of their compounds in the two coals. It is also conceivable that the mild oxidation prevailing during pretreatment (of Illinois No. 6 only) may additionally play a role in their behavior.

E. Conclusion

This study along with many other recent investigations into the behavior and distribution of trace elements in the production of synthetic fuels, constitute only a beginning. There is enough reliable information generated, as a result of this study, to indicate the need for an expanded program in this area. Much more comprehensive programs than the present effort are needed in order to compile adequate information for the proper design of the critically needed supplemental fuel plants.

CHAPTER II: ANALYTICAL METHODS

Identification of Instrumentation

The following instruments were used in this work:

Plasma Machine, Model IPC 11038 by International Plasma Corporation.

Atomic Absorption Spectrophotometer Model 303 with a background compensator installed internally by Perkin-Elmer Corporation.

Atomic Absorption Spectrophotometer Model 3038 by Perkin-Elmer Corporation.

Graphite Furnace, Model HGA-2000 by Perkin-Elmer Corporation.

Three-Meter, Grating Emission Spectrograph by Baird-Atomic Corporation

Spectrophotometer, Model DB by Beckman, Inc.

Research pH Meter, Model 13 by Corning Corporation.

Fluoride Specific Ion Electrode by Corning Corporation.

Calomel Fiber-Junction Reference Electrode by Corning Corporation.

Digital Volt-Ohm-Milliampere Meter, Model 460 by Simpson, Inc.

Sample Preparation

A. Size Reduction

All coal and residue samples were air dried and were crushed to pass an 80 - mesh sieve.

B. Organic Matter Removal

Several methods are available to prepare coal samples for trace elements analysis. The first step in each technique usually involves the destruction of the organic material in the coal. One method of organic material destruction is the high temperature ashing (HTA) process, by which, the sample is ashed in a muffle furnace at 400 to 800°C, resulting in the rapid oxidation of the organic material. Significant losses of volatile trace elements such as arsenic, selenium, cadmium, and antimony during HTA, make this process unacceptable for the analysis of these elements. The wet oxidation method, on the other hand, will introduce additional contaminants because of the large quantities of mineral acids used in the sample digestion.

The low temperature ashing (LTA) process removes the organic matter by plasma oxidation, at 1 mm oxygen pressure, and low temperature (<110°C). This method is the most effective way to achieve the oxidation of organic matter without introducing additional contaminants or undue loss of volatile trace elements. Some trace elements will be lost even during LTA, such as mercury, sulfur, nitrogen, and chlorine, which must be analysed in whole coal samples by other suitable methods.

The details of the low temperature ashing technique have been described in several publications [1,2,3,4]. For this study, we have followed the LTA procedure that was developed for our earlier work[4] on bituminous coal samples, except that the power input had to be increased from 15 watts/coil (used on bituminous samples) to 20 watts/coil for lignite samples, in order to maintain the LTA temperature at or below 115°C for the oxidation of organic matter.

C. Sample Dissolution and Analysis

Since there were nearly 40 elements to be analysed, no single dissolution procedure was found to be suitable for the entire list of elements. In fact, certain refractory elements were analysed directly in the LTA ash samples by emission spectroscopy. The bulk of the elements, however, were divided into four convenient categories or groups according to their particular analytical requirements as outlined in Tables 10 and 11.

1. Category I Elements

Care was taken to insure that better than 95% of initial organic matter in the coal samples were driven off by the LTA ashing before the addition of concentrated $HClO_4$ to the samples to prevent explosion.

A 0.5 g sample of LTA ash was weighed into a 100 ml Teflon beaker followed by the addition of 20 ml conc. HNO_3 and 5 ml conc. $HClO_4$. The beaker was heated gently until the initial reactions had subsided and the solution had become clear, indicating the complete oxidation of any residual organic matter. The beaker was removed and allowed to cool, rinsing the cover with a few ml of deionized water followed by the addition of 10 ml 49% HF. The heating was applied again until nearly all of $HClO_4$ was driven off. The beaker was, next removed from the hot plate and allowed to cool

Table 10. [illegible]

Categories	Methods of Sample Dissolution	Elements
I	Dissolution by $HClO_4$ – HF treatment. Here per a HCl matrix.	Li, Be, B, Sc, Mg, Ca, Ti, V, Cr, Mn, Mo, Fe, Co, Ni, Cu, Zn, Cd, Pb, and Bi
II	Dissolution by H_2SO_4 – HNO$_3$ treatment. Here per a H_2SO_4 matrix.	As, Sr, Te, Sb, and Sn
III	Analyzed by Emission spectrography without a sample dissolution step.	Zr, Ge, Th, and Ce
IV	Individual methods required for sample dissolution.	Ag, B, Ba, F, Hg, Cl, P, S, Si, and Tl

Table 11. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF SOLID SAMPLES

Constituent	Method	Detection Limit[b]	Range[c]	Precision, %[d]
Antimony	1. LTA-acid dissolution[a] Iodide-benzene extraction Flameless AAS	0.001 ppm	0.04-2 ppm	5
	2. LTA-acid dissolution[a] Hydride formation Heated-quartz-cell AAS	0.001 ppm		3
Arsenic	1. LTA-acid dissolution[a] Flameless AAS	0.01 ppm	1.0-10 ppm	7
	2. LTA-acid dissolution[a] Ion-exchange column separation APCD-MIBK extraction Air-C_2H_2 flame AAS	0.05 ppm		5
	3. LTA-acid dissolution[a] Ion-exchange column separation APCD-MIBK extraction Flameless AAS	0.001 ppm		7
	4. LTA-acid dissolution[a] Hydride formation Heated-quartz-cell AAS	0.001 ppm		3
Barium	1. HTA-acid dissolution[a] N_2O-C_2H_2 FES	0.01 ppm	20 ppm - 2%	5
	2. HTA-acid dissolution[a] H_2SO_4 ppt NH_4OH-EDTA redissolution N_2O-C_2H_2 FES	0.001 ppm		4
	3. HTA-Na_2CO_3 fusion[a] Hot-water leaching HCl dissolution N_2O-C_2H_2 FES	0.001 ppm		4
Beryllium	1. LTA-acid dissolution[a] N_2O-C_2H_2 AAS	0.002 ppm	0.2-2 ppm	7
	2. LTA-acid dissolution[a] Flameless AAS	0.0001 ppm		5
Bismuth	LTA-acid dissolution[a] APCD-MIBK extraction Flameless AAS	0.02 ppm	0.2-2 ppm	5

Table 11, Cont'd. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF SOLID SAMPLES

Constituent	Method	Detection Limit[b]	Range[c]	Precision, %[d]
Boron	LTA-Na_2CO_3 fusion[a] Diol-$CHCl_3$ extraction N_2O-C_2H_2 FES	0.05 ppm	10-500 ppm	5
Cadmium	1. LTA-acid dissolution[a] APCD-MIBK extraction Air-C_2H_2 flame AAS	0.005 ppm	0.1-10 ppm	4
	2. LTA-acid dissolution[a] APCD-MIBK extraction Flameless AAS	0.0001 ppm	1-50 ppm	5
Calcium	LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.002 ppm	0.1%-2%	3
Chlorine	Eschka-HNO_3 extraction[55] Amperometric titration	1 ppm	0.01% - 0.5%	8
Chromium	LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.01 ppm	10-500 ppm	4
Cobalt	1. LTA-acid dissolution[a] Flameless AAS	0.001 ppm	1-50 ppm	5
	2. LTA-acid dissolution[a] APCD-MIBK extraction Flameless AAS	0.0001 ppm		6
Copper	LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.01 ppm	5-50 ppm	3
Fluorine	Oxygen Bomb - SIE[a]	0.1 ppm	10-100 ppm	9
Germanium	LTA-emission spectrography	1 ppm	1-40 ppm	10
Iron	LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.005 ppm	0.2% - 5%	2
Lead	1. LTA-acid dissolution[a] APCD-MIBK extraction Air-C_2H_2 flame AAS	0.01 ppm	2-50 ppm	4
	2. LTA-acid dissolution[a] APCD-MIBK extraction Flameless AAS	0.001 ppm		6
Lithium	LTA-acid dissolution[a] N_2O-C_2H_2 FES	0.001 ppm	2-50 ppm	3

Table II, Cont'd. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF SOLID SAMPLES

Constituent		Method	Detection Limit[b]	Range[c]	Precision, %[d]
Magnesium		LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.001 ppm	0.02% - 1%	2
Manganese		LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.01 ppm	5-100 ppm	3
Mercury		Total combustion - $KMnO_4$[e] Cold vapor flameless AAS	0.1 ppb	0.01-5 ppm	10
Molybdenum		LTA-acid dissolution[a] Flameless AAS	0.005 ppm	1-10 ppm	6
Nickel		LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.01 ppm	10-50 ppm	4
Nitrogen		Kjeldahl digestion - titration[f]			
Potassium		LTA-acid dissolution[a] Air-C_2H_2 FES	0.001 ppm	0.02%-0.2%	3
Samarium		LTA-emission spectrography[a]	0.5 ppm	0.5-2 ppm	10
Selenium	1.	LTA-acid dissolution[a] Flameless AAS	0.01 ppm	0.1-50 ppm	6
	2.	LTA-acid dissolution[a] Ion-exchange column separation APCD-MIBK extraction Flameless AAS	0.001 ppm		5
Silicon	1.	LTA-gravimetric method[a]	0.1 mg	1%-5%	2
	2.	LTA-acid digestion bomb[a] N_2O-C_2H_2 flame AAS	0.1 ppm		3
Silver		LTA-acid dissolution[a] Flameless AAS	0.001 ppm	0.1-5 ppm	6
Sodium		LTA-acid dissolution[a] Air-C_2H_2 FES	0.005 ppm	0.01 - 0.2 ppm	3

Table 11, Cont'd. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF SOLID SAMPLES

Constituent		Method	Detection Limit[b]	Range[c]	Precision, %[d]
Strontium		LTA-acid dissolution[a] N_2O-C_2H_2 FES	0.001 ppm	10-500 ppm	3
Sulfur		Eschka-gravimetric method[f]	0.1 mg	0.1% ~ 5%	2
Tellurium	1.	LTA-acid dissolution[a] Flameless AAS	0.01 ppm	0.1 ~ 10 ppm	6
	2.	LTA-acid dissolution[a] Ion-exchange column separation APCD-MIBK extraction Flameless AAS	0.001 ppm		5
Thorium		LTA-acid dissolution[a] Ion-exchange column separation Colorimetric method	0.02 ppm	0.1 ~ 5 ppm	6
Tin	1.	LTA-acid dissolution[a] Iodide-isopropyl/ether extraction Flameless AAS	0.01 ppm	0.1 ~ 5 ppm	6
	2.	LTA-acid dissolution[a] Hydride formation Heated-quartz-cell AAS	0.01 ppm		5
Titanium		LTA-acid dissolution[a] N_2O-C_2H_2 flame AAE	0.1 ppm	0.01% ~ 0.1%	4
Vanadium	1.	LTA-acid dissolution[a] N_2O-C_2H_2 flame AAS	0.2 ppm	10-100 ppm	10
	2.	LTA-acid dissolution[a] Ion-exchange column separation APCD-MIBK extraction N_2O-C_2H_2 flame AAS	0.01 ppm		5
Ytterbium		LTA-emission spectrography[a]	0.1 ppm	0.1-1 ppm	10

Table 11, Cont'd. ANALYTICAL METHODS FOR CHEMICAL ANALYSIS OF SOLID SAMPLES

Constituent	Method	Detection Limit[b]	Range[c]	Precision, %[d]
Zinc	LTA-acid dissolution[a] Air-C_2H_2 flame AAS	0.01 ppm	0.1-100 ppm	6
Zirconium	LTA-emission spectrography[a]	1 ppm	10-100 ppm	10

Abbreviations:

AAS = Atomic absorption spectrophotometer
APCD = Ammonium pyrrolidine carbodithioate
Diol = 2-ethyl-1,3-hexanediol
EDTA = Ethylenediamine tetraacetic acid
FES = Flame emission spectrophotometer
HTA = High-temperature ashing
LTA = Low-temperature ashing
MIBK = Methylisobutyl ketone
SIE = Selective ion electrode.

Notes:

[a] Methods currently in use at IGT.

[b] Detection limits are estimated as the concentration of the constituent in the sample solution or mixture that would produce a signal twice as large as the background noise level. In gravimetric methods, detection limits are expressed as the minimum weight the balance can accurately weigh (0.1 mg in IGT's Analytical Laboratory).

[c] The range refers to the estimation of the constituent concentration in the sample.

[d] Precisions are estimated by applying the specified analytical method to the sample in the estimated range.

before adding 5 ml of 6M HCl plus 30 ml of water and gently reheating the content until the solution became clear. After cooling the solution the contents were quantitatively transferred to a 50 ml volumetric flask and brought up to mark with deionized water for analysis by one of several atomic absorption (or emission) methods, depending on the particular element being sought.

The Category I elements were further divided into three sub-groups A, B, and C, according to differences in the methods for their determinations.

Sub-group A included those elements which could be determined by direct aspiration into a flame, namely Li, Na, K, Mg, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Ti, and V. In this group, Li, Na, and K were determined by air-C_2H_2 emission flame photometry, since they have higher sensitivity by the flame emission method than flame atomic absorption method[5]. In order to suppress the ionisation effect, 1000 ppm of Cs was added to all the standard and sample solutions. Operational parameters for these elements are given in Table 13.

Mg, Ca, Cr, Mn, Fe, Ni, Cu, and Zn were determined by air-C_2H_2 flame atomic absorption spectrophotometry (AAS). One thousand ppm of lanthanum was added to all the standard and sample solutions, in order to eliminate the possible chemical interferences from the sample matrix with the determination of Ca and Mg.

Ti and V were determined by N_2O - C_2H_2 flame AAS. The operational parameters are given in Table 13.

Sub-group B, consists of Be, Co, and Mo, which were determined by direct introduction of the sample solution (or its dilution) into the graphite furnace, and quantified by flameless atomic absorption.

The detection limits for Be and Co, using a graphite furnace, are about 0.0002 mg/ml and 0.006 mg/ml, respectively. Therefore, these two elements were measured in a very dilute sample solution with no significant matrix effect. On the other hand, Mo not having a very high sensitivity, even with

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NOTE: The maximum temperature which the teflon beaker can withstand is ~150°C, therefore, the hot plate should not be set higher than that.

Table 12. [illegible]

[illegible]

Element	Electron type	Mode	Wave Length	Spectral Band Width	Operational Range	Detection Limit (LOD)	Relative Standard Deviation (RSD)
			Å		ppm		
Ti	Arc-CH_4	Emission	498.8	0.13	0 – 2	0.001	3 – 5%*
Mn	Arc-CH_4	Emission	380.8	0.13	0 – 10	0.0005	~3%
Fe	Arc-CH_4	Emission	766.5	0.13	0 – 10	0.0005	~3%
Mg	Arc-CH_4	Absorption	285.2	0.6	0 – 1.0	0.0003	~2%
Ca	Arc-CH_4	Absorption	422.7	0.6	0 – 10	0.002	~2%
Ti	Nyt-CH_4	Absorption	364.3	0.6	0 – 50	0.1	~5%
V	Nyt-CH_4	Absorption	318.4	0.6	0 – 5.0	0.02	~2%
Cr	Arc-CH_4	Absorption	357.9	0.6	0 – 5.0	0.005	~5%
Mn	Arc-CH_4	Absorption	279.5	0.6	0 – 10	0.002	~3%
Fe	Arc-CH_4	Absorption	248.3	0.2	0 – 10	0.005	~2%
Ni	Arc-CH_4	Absorption	232.0	0.2	0 – 5	0.005	~5%
Cu	Arc-CH_4	Absorption	324.8	0.6	0 – 10	0.005	~2%
Zn	Arc-CH_4	Absorption	213.9	0.6	0 – 2.0	0.002	~3%

* In figure samples (where content is much lower than in the transmission samples and the RSD is higher for figure samples.

Total Length	400 mm
Diameter	OD – 0.65 mm from Tip – 1.3 mm
Tip Opening	0.03 to 25 mm

the graphite furnace, had to be measured in the original sample solution without further dilution. The standard addition method was used to offset the matrix effect. Furthermore, because of the memory effect, the graphite cell was cleaned between runs (especially following a high conc. Mo solution) at the maximum temperature of the furnace until the baseline returned to the proper place. The background corrector was used for all the measurements, using the graphite furnace in order to compensate for any unspecific molecular absorption. The operational parameters for Be, Co, and Mo are given in Table 13.

Sub-group C, consist of Bi, Cd, and Pb which may be determined following solvent extraction by aspirating the organic phase into a flame, or by introducing the organic phase into the graphite furnace. In most cases, the use of the graphite furnace required the use of the standard addition method, which was not only tedious but less precise. Using extraction as a separation method, it was possible to eliminate the matrix effect in the graphite furnace and also to pre-concentrate the sub-group C elements.

Bi, Cd, and Pb were separated from the major constituents in the sample solution by a simple solvent extraction[7,8], using sodium diethyldithiocarbamate or the ammonium pyrrolidinecarbodithioate as the chelating agents. These ions were quantitatively extracted into methylisobutylketone (MIBK) in a single pass extraction. With approximately 20 ml of the original sample solution extracted into 5 ml MIBK, Pb and Cd were determined by direct aspiration into an air-C_2H_2 flame. However, since the sample solution was not available in sufficient quantity, the graphite furnace was used for their determinations. One ml of acid solution was extracted into 5 ml of MIBK to recover Pb and Cd, and 5 ml of sample solution was extracted into 5 ml of MIBK for Bi determinations. The operational parameters of the instrument are present in Table 13.

| | | |

2. Category II Elements

As shown in Table 14 the fluorides of arsenic, selenium, and tellurium have moderate to high volatilities. Therefore, instead of $HF-HClO_4$ acids a mixture of $HNO_3 - H_2SO_4$ acids was used to prevent the loss of these elements during sample decomposition and dissolution.

Sample dissolution was accomplished by weighing a 0.5g of LTA sample into a glass beaker and adding 20 ml of conc. HNO_3 and 5 Ml selenium-free sulfuric acid.* The beaker was covered and heated gently for about one hour, followed by a second period at higher heating until the sulfuric acid fumes had appeared and the solution had turned clear. Next, 5 ml of deionized water were added and the solution was heated to white fumes again. Then 30 ml of deionized water were added, the solution boiled, filtered into a 50 ml volumetric flask and brought up to 50 ml mark.

Arsenic, selenium and tellurium were determined by introducing the sample solution or its dilution directly into a graphite furnace and making the measurements. The operational parameters for these elements are given in Table 15.

Antimony was extracted as its iodide[11,12], using benzene. An aliquot of the sample solution containing approximately 0.1 ug of antimony was placed in a centrifuge tube. The sulfuric acid concentration was adjusted to 9M, and sufficient KI was added so that the final volume had a concentration of 0.01 M in KI. The final volume of the sample solution was adjusted to 5 ml, then 0.5 ml of benzene was added by a micropipet. The solution was then shaken vigorously for one minute and centrifuged, retaining the benzene phase for the determination of antimony by graphite furnace.

Tin was extracted from acid solutions with 1.5 M KI and 1.5 M H_2SO_4 into an isopropyl ether solution[13], thus extracting the tin in ether layer for determination in the graphite furnace. The operational parameters for these elements are given in Table 16.

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*NOTE: Selenium-free sulfuric acid is prepared by diluting 150 ml concentrated H_2SO_4 with 150 ml deionized water, adding 15 ml HBr and boiling until the volume is reduced to less than 200 ml.

TABLE 14. BOILING POINTS OF As, Se, Te, Sb and Sn FLUORIDES[10]

Compound	Boiling Point, °C
AsF_3	-60
AsF_5	-8.5
SeF_6	-34.5
SeF_4	>100
TeF_6	35.5
TeF_4	>97
SbF_3	319 Subl
SbF_5	147.5
SnF_2	--
SnF_4	705 Subl

| | | |

3. Category III Elements

The compounds of the elements belonging to this group were either difficult to bring into solution, or were present at such low concentrations that the dissolution step would have diluted them beyond the sensitivity of the instrument used for their measurement. Group III elements include Ge, Sm, Yb, and Er.

Arc-emission spectrography was used for their determinations. This method had the following advantages: 1) Acid dissolution was not necessary, 2) The sensitivity was high enough for the determination of these elements, 3) It offered speed of operation. Usually, any emission spectrographic method for a particular kind of sample requires a certain amount of time for method development and set-up. Since a relatively small number of samples required this analysis, the standard addition method was used to offset the interferences from sample matrix. The analytical line pairs are given in Table .

Table 16. ANALYTICAL LINE PAIRS FOR GROUP III ELEMENTS

Ge	303.91nm / Fe 303.79 nm
Sm	442.43 nm/ Fe 441.51 nm
Yb	398.80 nm/ Fe 400.53 nm
Er	360.12 nm/ Fe 365.15 nm

One part of the LTA ash sample was mixed with two parts of spectrochemically pure graphite powder, containing known amounts of each element sought. The electrodes were National Spectrographic Laboratory 1400 cratered electrode and 13951 round top counter electrode. The mixture was loaded into a cratered electrode with a spatula, and made into a cone shape with a sharpened graphite rod. The 3 mm wide analytical gap was surrounded by an 80% argon and 20% oxygen atmosphere from a Stallwood jet in order to eliminate CN band emission. The conditions for arcing were 10 sec pre-arcing at 5 amp, 50 sec arcing at 10 amp, and then 60 sec arcing at 15 amp. The pre-arcing step was important because the LTA sample still contained some residual carbonaceous matter, which would have volatilized first, resulting in a high background reading.

The photographic plate was developed in Eastman D-19 Developer for 3 min and fixed for another 3 min in Eastman Fixer with a cold tap water rinse in between. The temperature of the developer and the fixer was kept constant with a water bath.

4. Category IV Elements

The procedures for the sample preparation and determination of elements in this group have been developed for each element individually. Elements in this group are: Hg; F; B; Ba; Si; Ag; Cl; and Th.

Many methods are available for the determination of mercury[13-19], however, the flameless atomic absorption method (with minor modifications) was adopted for this study. A one-g sample of whole coal was burned in an ASTM carbon-hydrogen train with CuO as the only packing material. Mercury vapors were collected from the combustion effluents in an absorbing solution containing 1% $KMnO_4$ in 0.1 N H_2SO_4, which was then reduced by a solution made up by dissolving 4 g $SnCl_2$ and 2 g NH_2OH in concentrated HCl and then diluted to 100 ml.

The absorbing solution and other reagents were checked prior to use to make certain that there was no detectable amount of mercury present as contaminant. Before the operation, the carbon-hydrogen train was purged overnight with mercury-free oxygen at a flow rate of 20 ml/min at the operating temperature. Blank runs were made to make sure that combustion train was free from contamination.

Following the combustion, an aliquot of the absorbing solution, containing less than 20 nanograms of mercury was drawn into a 50 ml plastic syringe. Water was added to bring the total volume to 10 ml, followed by the addition of 5 ml of the reducing solution. Clean air was drawn in to give a total gas volume of 30 ml in the syringe. The syringe was capped and shaken vigorously for 30 seconds, then the vapor contents were injected into the cell, taking care not to inject any solution. After tracing the signal for 5-15 seconds, the air was drawn back into the syringe from the cell and the cell was purged with air so that recorder pen returned to the baseline.

Fluorine was determined in whole coal by an oxygen-bomb combustion and selective ion electrode method[19,20]. A 1g sample of -60 mesh coal was weighed in a stainless steel container, and then fired in an oxygen bomb, charged with 30 atm of oxygen and 10 ml 0.05 N NaOH. After firing, the bomb was cooled, depressurized, and sample solution was transferred to a 50 ml glass beaker. The bomb was rinsed thoroughly with three 5 ml portions of 0.05 N NaOH, adding the rinsings to the sample solution. The total solution was heated gently on a hot plate to expell dissolved CO_2 and O_2, then transferred to 25 ml volumetric flask and diluted to volume.

Ten ml of sample solution was mixed with 10 ml of a buffer solution, made by mixing 57 ml of acetic acid and 58 grams sodium chloride with 4 grams of cyclohexanediamine-tetra-acetic acid. The pH was adjusted to 5.3 and the final volume brought to 1 liter.

The measurements were made using a fluoride-ion electrode against a reference electrode. A research pH meter on mV mode was used as the readout. The standard addition method was used by adding 20 and then 40 mg of fluoride to the solution after the initial measurement was made. The concentrations were read from a standard curve and the percent recovery calculated from the concentrations.

In earlier work, boron in coal was determined by emission spectrographic method. However, since then, the extraction of boron by 2-ethyl-1, 3-hexanediol into an organic solvent and subsequent determination by $H_2O - H_2$ flame emission spectrophotometry[22,23,24] was found to be a simpler procedure. It was also comparable to colorimetric methods in its precision and sensitivity, but easier to follow.

The LTA sample was used for boron determination, because there are many contradictory statements in the literature concerning the gains and losses of boron during the high temperature ashing process. However, a few samples ashed at 500 °C in this laboratory and analysed for boron, showed comparable results with LTA ash samples.

A mixture of 0.2 grams LTA sample and 3 grams of Na_2CO_3 was fused on a blast burner for 5 to 10 minutes, and dissolved in the proper amount of HCl. The total sample solution was adjusted to 30 ml in a plastic separatory funnel. Ten ml of a 1:9 solution of 2-ethyl-1, 3-hexanediol in chloroform was added to the separatory funnel. After the extraction of boron by the organic phase, the chloroform was drained from the bottom of the funnel and aspirated into a $N_2O - H_2$ flame, with a flow rate of 12 l/min for both gases. Using a 5 cm slot burner head the emission of BO_2 was measured at 518.8 nm. The slit width was set at 4 on the Perkin-Elmer 305B Atomic Absorption Spectrophotometer corresponding to 0.6 nm of the spectral band width. A blank solution was also aspirated between the sample solutions, using zero suppression to adjust the baseline.

The determination of the Ba in solution, using an emission $F_2O - C_2H_2$ flame was relatively easy[26,27]. The sample dissolution for the determination of barium in coal samples, however, presented a unique problem due to the wide range of the barium contents in coal samples and very low solubility of the barium sulfate in acid solution.

The direct acid dissolution of LTA samples of lignite by $HClO_4 - HF$ treatment was not satisfactory and gave low results. Because of the low concentration of barium in bituminous samples, the HTA sample could be dissolved by $HClO_4 - HF$ acid treatment provided that the sample size was kept smaller than 0.1g and the final volume was at least 100 ml.

The lignite samples were dissolved in sulfuric acid and recovering the barium as barium sulfate. The barium sulfate was redissolved either by ethylenediamine tetra acetic acid[25] or by fusion with sodium carbonate followed by aqueous leachings to separate the sulfate from the barium and dissolution of the barium carbonate in hydrochloric acid.[26] These methods were found to be adequate for the determination of barium by $N_2O - C_2H_2$ flame emission. The background emission, however, caused by the large amounts of Ca in the solution as CaOH was corrected by measuring both sides of the barium 553.5 nm emission line. The average of the measurements was then used to correct the measurement made at the 553.5 nm Ba emission line.

Silicon was determined either by the classical gravimetric method using HF devolatilization method, or by $N_2O - C_2H_2$ flame atomic absorption spectrophotometry following the Parr acid-digestion bomb treatment. These two methods gave comparable results, but the atomic absorption method was preferred because it was less time consuming.

In the acid-digestion bomb method for Si, 0.1 g of LTA sample was put in a 25 ml Parr acid-digestion bomb with 3 ml HNO_3 (conc.) and 0.5 ml HF (48%). The bomb was tightly closed by hand and placed in an oven at 150 °C for 1-2 hours. The bomb was then, removed from the oven and cooled to room temperature and opened carefully. A 10 ml volume of a saturated boric acid solution was next added to the contents to react with excess HF acid. The sample solution was transferred to a 100 ml plastic volumetric flask and brought to volume with deionized water. A series of standard solutions were also prepared in the same acid matrix, and their absorption signals were measured at 251.6 nm.

The determination of Ag was accomplished by the graphite furnace/atomic absorption method. The LTA sample was dissolved by $HClO_4$ - HF treatment, followed by HNO_3 instead of HCl, to prevent precipitation of AgCl. All glassware were carefully rinsed with 3 N HNO_3 and deionized water to remove traces of chloride ion. The sample solution was then introduced directly into a graphite furnace. The operational parameters are listed in Table 17.

Chlorine was measured by Eschka/amperometric titration method. The sample preparation steps followed the ASTM method. The filterate from Eschka procedure, was titrated amperometrically against 0.005 N $AgNO_3$ solution, using 20 ml of sample solution, 5 ml acetone, and 5 ml 1% gelatin solution. Nitrogen was passed through the solution for at least 5 minutes before the titration had begun.

Thorium was determined by a colorimetric method after the separation of thorium by extraction with trifluorothenoyl acetone (TTA), and back-extraction.[29] The iron (III) which interferred with the extraction of Th in TTA was first removed by extraction with isopropyl ether from a 6 N HCl solution.

The thorium so separated was then reacted with thorin, and its absorbance was measured in spectrophotometer at 545 nm with a 5 cm cell. A zero standard was used as reference blank.

Table 17. OPERATIONAL PARAMETERS FOR THE DETERMINATION OF Ag.

	Wave Length (nm)	Spectral Band Width (nm)	Operation Range (ng/ml)	Drying Cycle	Ashing Cycle	Atomising Cycle	RSD[a]
Ag	328.1	0.5	0 – 9.1	130 °C-60 Sec	500 °C-60 Sec	2400 °C-5 Sec	5%

[a] Relative standard deviation

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